Torsional properties of boron nitride nanocones with different cone heights, disclination angles and simulation temperatures

Yuan Li[1], Yanling Tian[1*], Chengjuan Yang[1], Kunhai Cai[1], Dawei Zhang[1]

[1]*School of Mechanical Engineering, Tianjin University, Tianjin 300072, China*

**Author to whom correspondence should be addressed. Electronic mail: meytian@tju.edu.cn*

Abstract

The torsional properties of single-walled boron nitride (BN) nanocones at different cone heights, disclination angles and simulation temperatures have been investigated using molecular dynamics (MD) simulation. The simulation results indicate that the torque and average potential energy decrease with the increasing cone height and disclination angle, and the failure torsion angle increases with the increasing cone height and disclination angle. For different simulation temperatures, the torsional behavior of BN nanocones at higher simulation temperature is more serious and earlier to reach a failure point, the maximum torque and average potential energy of the system decrease with the increasing simulation temperature. For different loading rates, the failure torsion angle decreases with the increasing loading rate, so the fracture of BN nanocone is occured earlier with higher loading rate. Therefore, the cone height, disclination angle, simulation temperature and loading rate are considered to be four main influencing factors for the torsional properties of the BN nanocones.

1. Introduction

The nanocones were discovered in 1992 as caps at the end of nanotubes[1]. Since the discovery about carbon fullerenes, nanotubes and nanocones, as curved nanostructures they attract investigators because of the excellent and unique mechanical, physical and electronic properties[2-4], The technologies of investigation about compositions and properties of

nanostructures based on carbon structures are constantly emerging through the applications of various theoretical and experimental means, and these technologies also show the huge applications of nanostructures in engineering science[5-7]. Similar to carbon nanocones, BN nanocones were proposed since 1994 and several years later were experimentally observed[8-11]. BN nanocones are also formed by rolling nanostructure sheet, and the electrical conductivity of BN nanocones is different with the different rolling direction and radius. However, as carbon counterparts, BN nanostructures are more attractive because of chemical oxidation inertness, mechanical toughness and thermal stability[12-13].

The characteristics of nanocones depend on the angle of the sector removed from a flat sheet to form a cone, namely, the disclination angle. For carbon nanocones, there are five disclination angles (60 °, 120 °, 180 °, 240 °and 300 °) and only C-C bonds. The BN nanocones have three types of covalent bonds; those are B-N, B-B, and N-N bonds[14], which result in the different physical, chemical, and electronic properties between carbon and BN nanostructures. The disclination angles of BN nanocones are the same with those of carbon nanocones, and those different disclination angles of BN nanocones have been synthesized experimentally[15-19]. Due to the existence of non B-N bonds in which disclination angles are 60 °and 300 °, these two types of BN nanocones are defective and the mechanical properties may be affected. In recent years, investigations for BN nanocones mainly about synthesizing various structures and observing electronic properties[20-21], but the mechanical properties are rarely penetrated into discussing which is very important for the applications of future, because of which, the study for the configurations and mechanical properties of BN nanocones under twisting shows important significance.

In this paper, the twisting phenomenon and torsional behavior of BN nanocones have been systematically explored using MD simulation. Tersoff potential was used to describe the

interaction of B-N bonds. The whole MD simulation process was carried out by Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). Initial model of BN nanocones used in LAMMPS calculation was supplied by Material Studio. The simulation of torsion of BN nanocones was performed based on the existed models and mature calculations. Finally, the effects of cone heights and disclination angles of BN nanocones on the energy and torque were investigated emphatically; in addition, the influence of temperature and loading rate on the torsional behavior also have been discussed in detail.

2. Modeling and simulation method

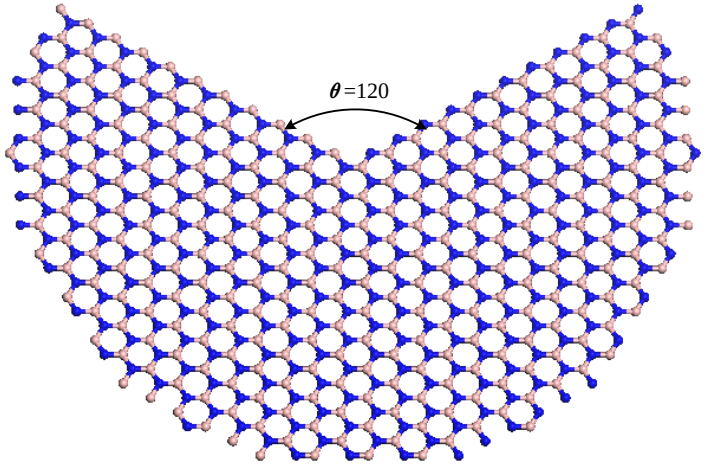

Fig. 1. The cone sheet for rolling BN nanocone.

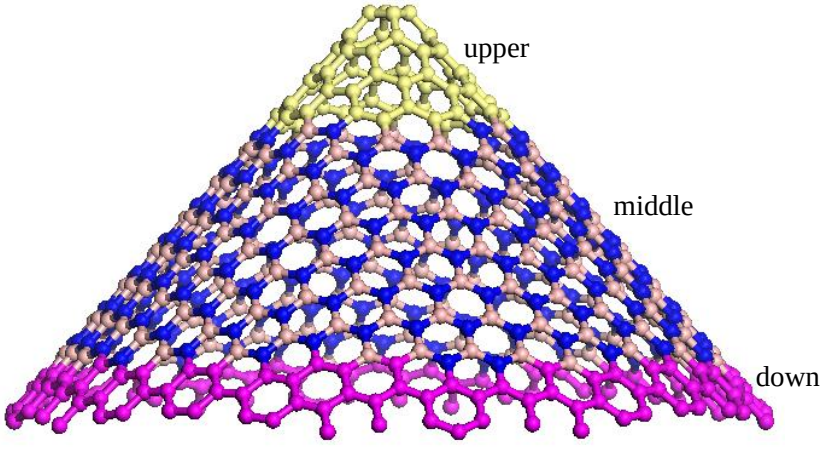

Fig. 2. The model of BN nanocone with 120 °disclination angle and its layers.

In the applications of BN nanocones, the mechanical properties of BN nanocones have significant practical value, among which the torsional properties play a crucial role. Therefore, the torsional properties are explored systematically in this study. Several types of cones with 60 °, 120 °, 180 °, 240 °, 300 ° disclination angles and 20Å, 30Å, 40Å cone heights were modeled by Material Studio, respectively. The cone with 60 ° disclination angle has a pentagonal ring at its apex and the cone has a defective line at its wall which is formed by B-B or N-N bonds. The cone with 120 ° disclination angle presents a square ring at its apex and the cone only has B-N bonds. The cone with 180 ° disclination angle presents a triangle ring at its apex. The cone with 240 ° disclination angle presents an apex formed by two atoms (B and N) at the top of an unusual hexagonal ring.[22].

The models of BN nanocones, for example, with 120 ° disclination angle in Fig. 2, can be obtained by rolling the nanocone sheet as shown in Fig. 1. The length of B-N bond is 1.45 Å[23]. In order to conduct the computational calculations, the entire nanocone has been divided into three regions (upper, middle, down) (Fig. 2). The down region is fixed to constrain the nanocone and the fixed height is 3 Å, the upper region is used to bear loads and the height is 8 Å, the middle region is free of constrain, where the positions and velocities of the atoms obey the Newton's second law. The atoms of upper region and down region are not subject to internal forces. However, they provide internal forces to the atoms in the middle region. NVT ensemble was employed in the molecular dynamics simulations, which can keep the number of atoms, volume and temperature constant. In order to reduce the temperature-induced fluctuation of atoms, the system temperature is set at 1K with the use of the Nose-Hoover thermostat algorithm[24]. The time step in the simulation is 1fs. The BN nanocone is completely relaxed for a certain period to minimize the internal energy and reach an equilibrium state before applying external load, then, a torsion control methodology is adopted to apply external load to the BN

nanocone, the atoms in top region of BN nanocone are twisted with the rate of 0.01degree/ps and meanwhile the atoms at the down region are fixed, so the torsional behavior of BN nanocone can be obtained. Tersoff potential included in LAMMPS software package was used to describe the interaction among atoms, when the program of LAMMPS is prepared with output parameters such as torque, average potential energy, etc, the characteristics of BN nanocones under twisting can be analyzed during this simulation.

The classic molecular dynamics method is used to study the torsional behavior of BN nanocones, which is based on the Tersoff potential as mentioned above. Tersoff potential function was used to describe the interaction among atoms in this study, the formula of which is expressed as follow:

$$E=\frac{1}{2}\sum_{i\neq j}V_{ij}=\frac{1}{2}\sum_{i\neq j}f_c\left(r_{ij}\right)\left[f_R\left(r_{ij}\right)+b_{ij}f_A\left(r_{ij}\right)\right] \tag{1}$$

$$f_C\left(r_{ij}\right)=\begin{cases}1 & r_{ij}<R_{ij}\text{-}D_{ij}\\ \frac{1}{2}-\frac{1}{2}\sin\left[\frac{\pi}{2}\frac{r_{ij}-R_{ij}}{D_{ij}}\right] & R_{ij}\text{-}D_{ij}<r_{ij}<R_{ij}+D_{ij}\\ 0 & r_{ij}>R_{ij}+D_{ij}\end{cases} \tag{2}$$

$$f_R\left(r_{ij}\right)=A\exp\left(-\lambda_1 r_{ij}\right) \tag{3}$$

$$f_A\left(r_{ij}\right)=-B\exp\left(-\lambda_2 r_{ij}\right) \tag{4}$$

$$b_{ij}=\left(1+\beta^n\zeta_{ij}^n\right)^{-\frac{1}{2n}} \tag{5}$$

$$\zeta_{ij}=\sum_{k\neq i,j}f_C\left(r_{ik}\right)g\left(\theta_{ijk}\right)\exp\left[\lambda_3^3\left(r_{ij}-r_{ik}\right)^3\right] \tag{6}$$

$$g\left(\theta_{ijk}\right)=1+\frac{c^2}{d^2}-\frac{c^2}{d^2+\left(h-\cos\theta\right)^2} \tag{7}$$

where f_C, f_R and f_A are cut off function, mutually exclusive atomic potential and attractive

atomic potential, respectively. r_{ij} is the distance between i and j , b_{ij} is command function of the atomic bonds, θ_{ijk} means the angle between i j bond and i k bond. These parameters can be derived by first-principles calculations and experimental data[25]. The parameters used in Tersoff potential are shown in Table 1.

Table 1. The parameters of Tersoff potential.

A(eV)	4570.8	c	1093.28
B(eV)	3732.28	B($\times 10^{-7}$)	1.1134
λ_1(Å^{-1})	2.99038	d	14.82145
λ_2(Å^{-1})	2.77618	h	-0.6815
λ_3(Å^{-1})	0	R(Å)	2.0
n	0.351653	D(Å)	0.1

3. Results and discussion

3.1 Cone height

In this study, the twisting phenomenon and torsional behavior of BN nanocones with different models have been analyzed. In order to study the influence of cone height and disclination angle on BN nanocones, firstly, three models with the same disclination angles of 120° and different cone heights of 20 Å, 30 Å and 40 Å were built to explore the influence of cone heights with simulation temperature of 1K, secondly, five models with the same cone heights of 30 Å and different disclination angles of 60°, 120°, 180°, 240° and 300° were set up to study the influence of disclination angles with simulation temperature of 1K. Thirdly, three models with the cone heights of 30 Å and disclination angles of 120°, but different simulation temperatures of 1K, 100K, and 200K were used to evaluate the effect of temperature. Finally, three models with the cone heights of 30 Å and disclination angles of 120°, but different loading rates of 0.005degree/ps, 0.01degree/ps and 0.02degree/ps were used to study the effect of loading rate.

Through MD simulation and data processing, the twisting phenomenon and torsional behavior of BN nanocones were characterized by the relationships between torsion angle and torque, torsion angle and average potential energy respectively.

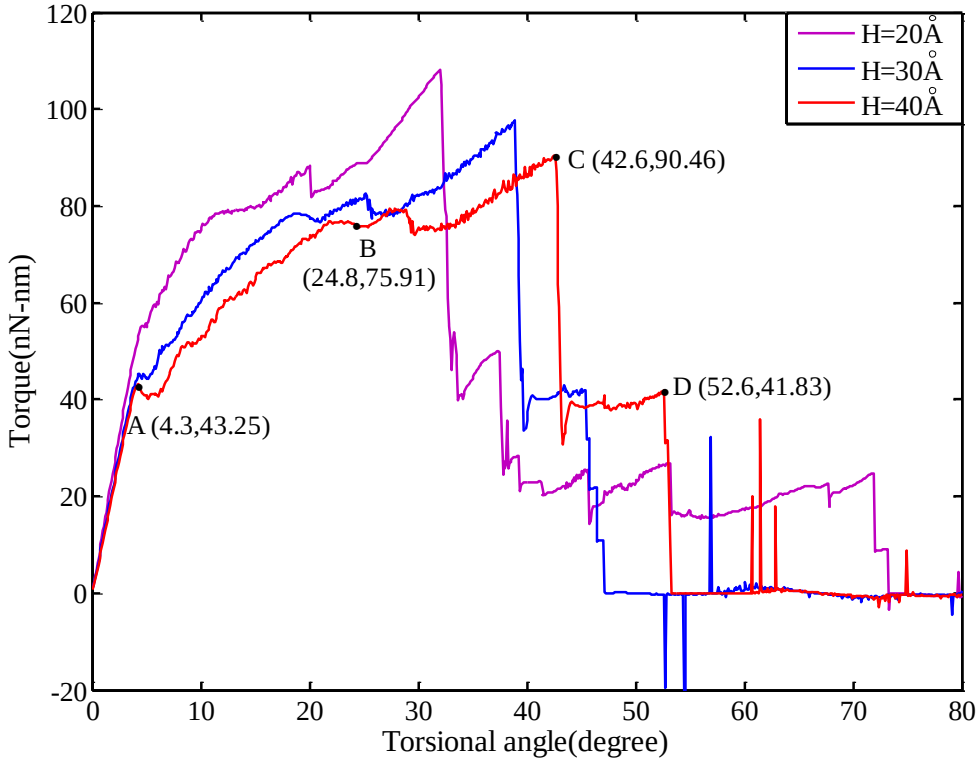

Fig. 3. The relationship between torsional angle and torque at different cone heights.

In order to discuss the deformation process in more detail, the BN nanocone with 40 Å was taken as an example. When the torsion angle increases to 4.3 °, the nanocone begins to lose its cone shell geometry and buckles into a twisted screw. Point A in Fig. 3 is the critical point for twisting, and the corresponding visual picture is shown in Fig. 4(A). Beyond critical point A, the structural integrity of BN nanocone will be destroyed including that B-N bonds break gradually and rearrange in some degree, which induces that the curve from A to C in Fig. 3 increases nonlinearly and has fluctuations up and down. Deformation in point B is shown in Fig. 4(B). Subsequently, when torsion angle is 42.6 °, the curve reaches at failure point C as shown in Fig. 3

and Fig. 4(C), corresponding torque at this point is largest and torsional behavior is the most serious. Once the curve passes point C, the structure of BN nanocone is destroyed completely as given in Fig. 3 and Fig. 4(D). The buckling deformation of BN nanocones under torsion has three stages (Fig. 3). In the initial stage, the resultant torques increase approximately linearly with the torsion angle increasing before reaching the critical torques. In the middle stage, as torsion angle increases, the torques increase nonlinearly and have some fluctuations prior to failure. In the last stage, at large torsion angles, all of the B-N bonds almost break and the torques decrease rapidly to about zero nonlinearly.

Fig. 3 also shows that the torque curves of BN nanocones with different cone heights have similar variation trend as the torsion angle changes, but the torsional capacities of which are different. The height is higher, the failure torsion angle is larger but the corresponding value of torque is smaller. Specifically, it is can be seen that the curve of 40 Å height deforms first and breaks last, the curve of 30 Å height deforms and breaks second, the curve of 20 Å height deforms last and breaks first. Therefore, it is concluded that the height is higher, the failure torsion angle is bigger and the maximum torque is smaller.

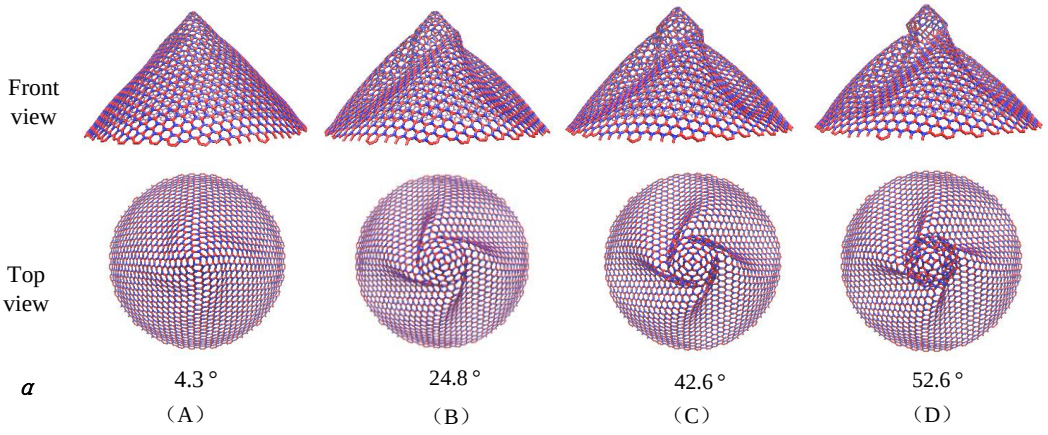

Fig. 4. The deformation process of BN nanocone with 120 °disclination angle and 40 Å heights.

To explore the torsional properties of BN nanocones further, the energy during torsion has

been studied and the relationship between torsion angle and average potential energy is given in Fig. 5. The average potential energy increases with the increasing torsion angle and then decreases quickly with some fluctuations when the torsion angle reaches failure point. Fig. 5 shows the average potential energy curves of BN nanocones with three different heights, it can be found that the curve of 20 Å height arrives to the highest point first and its average potential energy is maximum, the second is the curve with 30 Å height and the third is the curve with 40 Å height. So the cone height is higher, the maximum average potential energy of BN nanocone is smaller and increases more slowly, also the corresponding failure torsion angle is bigger. Similar to Fig. 3, the deformation process of points A, B, C and D on the curve of 40 Å has been shown in Fig. 4, respectively.

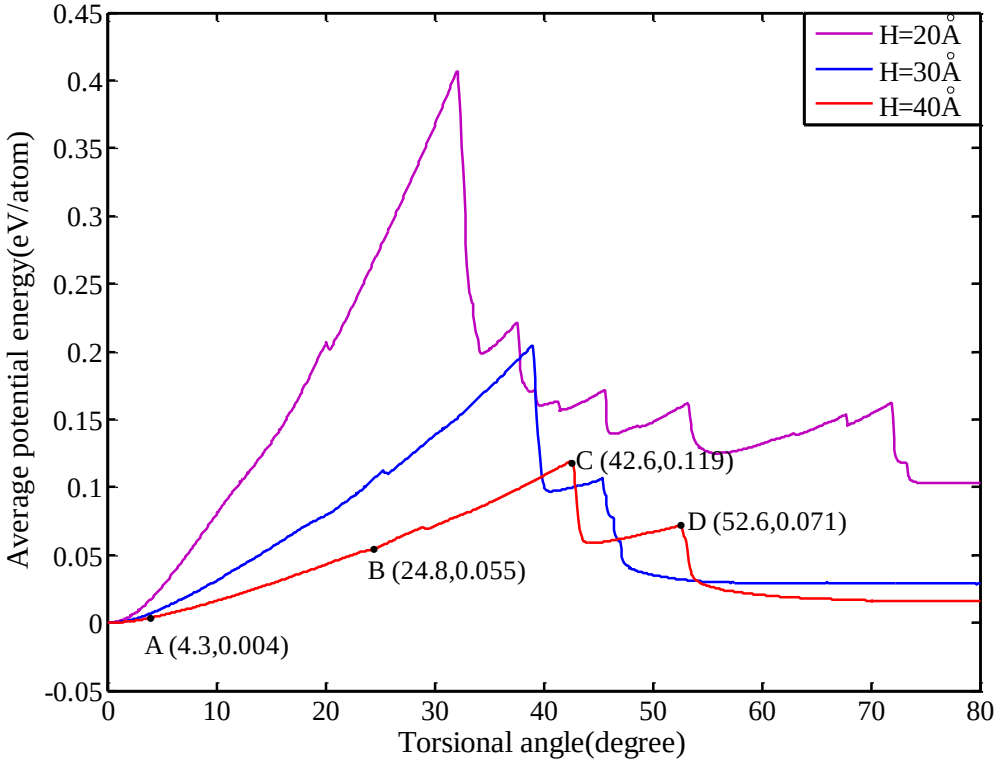

Fig. 5. The relationship between torsional angle and average potential energy at different cone heights.

3.2. Disclination angle

In this study, the torsional behavior of BN nanocones with different disclination angles also has been investigated in detail. From the relationship between torque and torsion angle shown in Fig. 6, it can be derived that the tendencies of these curves are the same with those curves of different heights. Overall, torque increases as the torsion angle increases. At the beginning, the torque increases linearly until the torsion angle passes the critical point then increases nonlinearly and slowly between the critical point and failure point of torsion angle, finally, the curve decreases quickly when the torsion angle passes the failure point. The main reasons of changing process formation are not only the fracture and rearrangement of the atomic bonds, but also the position modification of the atoms. Under the action of torsional force, the nanocone begins to twist and atoms also start to move along the torsional direction. The torque increases linearly until the atomic bonds begin to fracture. Once the torsion angle passes the critical point, the atoms start to move because of the fracture and rearrangement of the atomic bonds, so the torque increases nonlinearly at this stage. Beyond the failure point of the torsion angle, both atomic bonds and structure of the nanocone are destroyed completely; therefore, the torque decreases quickly to almost zero. And it can be seen that, with the increase of disclination angle, the curve is getting smoother and the failure value of torsion angle becomes bigger. On the contrary, the torque decreases with the increasing disclination angles. This result is similar to the torsional buckling of carbon nanocones with different disclination angles[26]. The snapshots of BN nanocones of 20° torsion angle with different disclination angles prior to failure have been shown in Fig. 7, it is not difficult to find that for the same torsion angle, the torsional behavior of the cone with 60° disclination angle is the most obvious and its corresponding torque is maximum. However, the nanocones with 240° and 300° disclination angles are both almost no reverse and their torque are very small. Consequently, when the nanocone with 60° disclination angle has already broken, the nanocone with 120° disclination angle will break, and the other

three are still twisting.

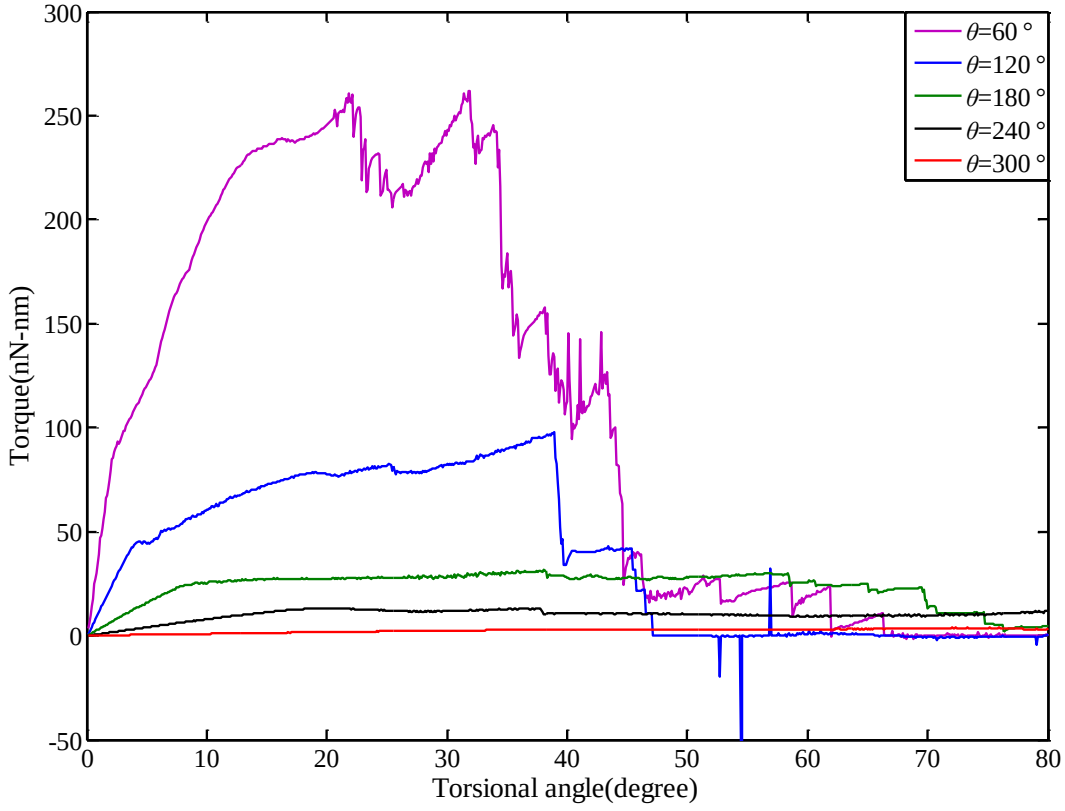

Fig. 6. The relationship between torsional angle and torque at different disclination angles.

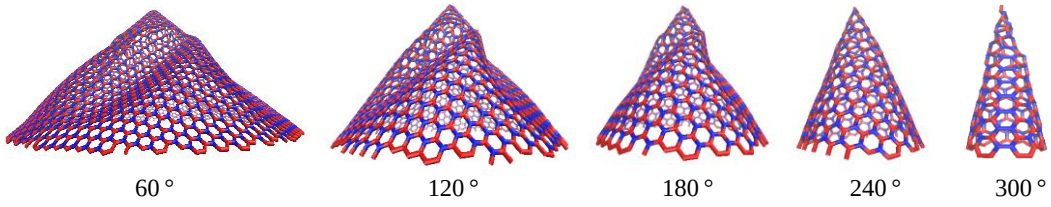

Fig. 7. The torsional behavior of BN nanocones with different disclination angles at the same torsion angle.

The relationship between average potential energy and torsion angle has been shown in Fig. 8. Average potential energy increases near linearly with the torsion angle increasing prior to failure, and then the average potential energy decreases quickly; sometimes there are sharp drops in energy curves due to the breaking of B-N bonds and a successive rearrangement. With the torsion

angle increase, the average potential energy of the nanocone with 60° disclination angle increases the fastest, and nanocone with 300° disclination angle increases the slowest. So the nanocone of 60° disclination angle first arrives at the failure point, the nanocone of 120° disclination angle is the second, third is the nanocone of 180° disclination angle, and the torsional processes of nanocones with 240° and 300° disclination angles are longer than others, so they need more time to reach to a failure point, and there is no regular about the maximum average potential energy of these nanocones. Therefore it can be derived that the disclination angle is bigger, the increase of average potential energy is slower, and the failure torsion angle is bigger.

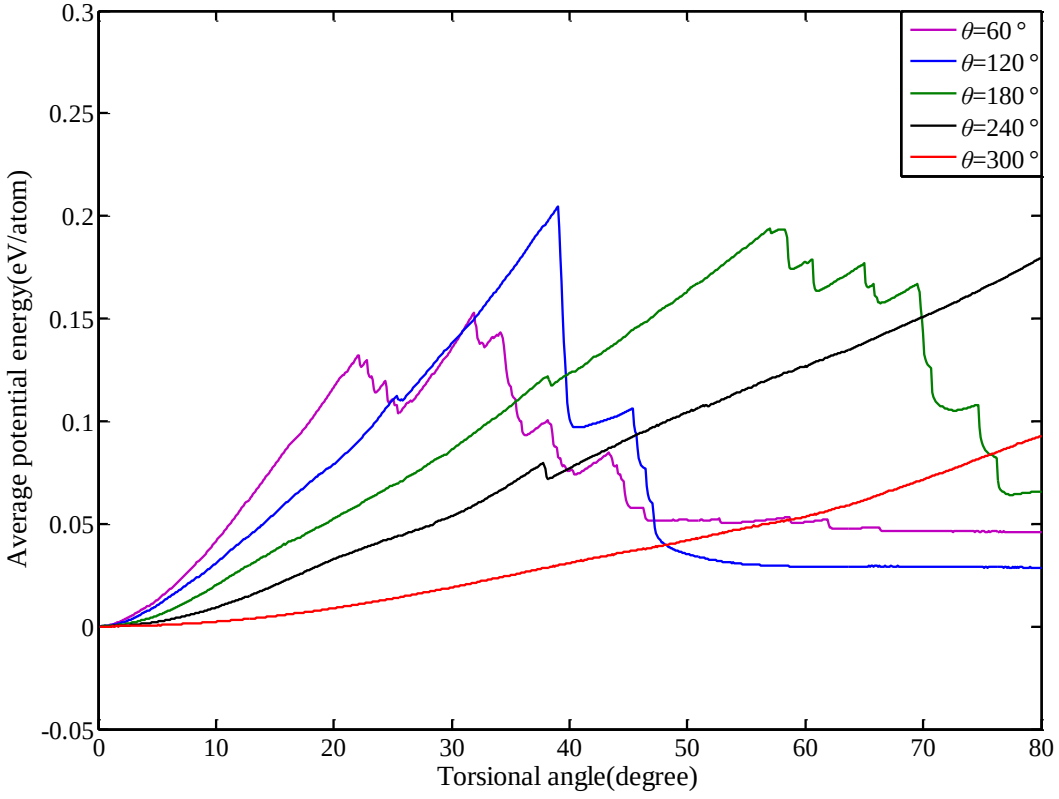

Fig. 8. The relationship between torsional angle and average potential energy at different disclination angles.

3.3. Temperature

In previous discussions, MD simulations carried out at constant temperature of 1K were used to investigate the effect of different cone heights and disclination angles on the torsional behaviors of BN nanocones. Furthermore the other MD simulations were performed at higher temperature of 100K and 200K in order to study the influence of temperature on the torsional behavior of BN nanocones. The relationship between the torsion angle and torque of BN nanocones at different temperatures is shown in Fig. 9, also curves for torsional angle and average potential energy at different temperatures are shown in Fig. 10. With the temperature increasing, the smoothness of the curve decreases and there are no distinct turning points due to the thermal fluctuation during twisting. As the temperature increases, atoms become more active and the fracture of the bonds occurs earlier, but there is no clear turning point in post buckling stage, and the fluctuations in the curves is due to the break and rearrangement of atomic bonds[27]. At the same time, as the twisting atoms move actively, the distance between atoms will become shorter which is beneficial to the capacity of rearrangement and also makes the decrements of torque and average potential energy of the system occur earlier. So it can be concluded that the torsional behavior of BN nanocones at high temperature is more serious and earlier to reach a failure point than that at low temperature, the maximum torque and average potential energy of the system decrease with the increasing simulation temperature.

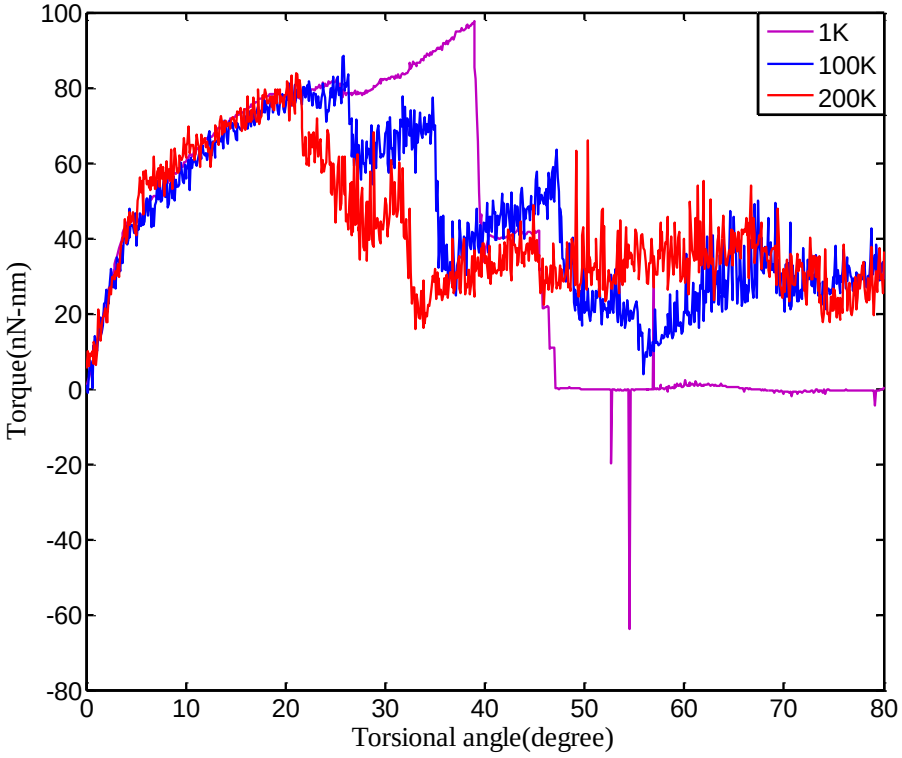

Fig. 9. The relationship between torsional angle and torque at different simulation temperatures.

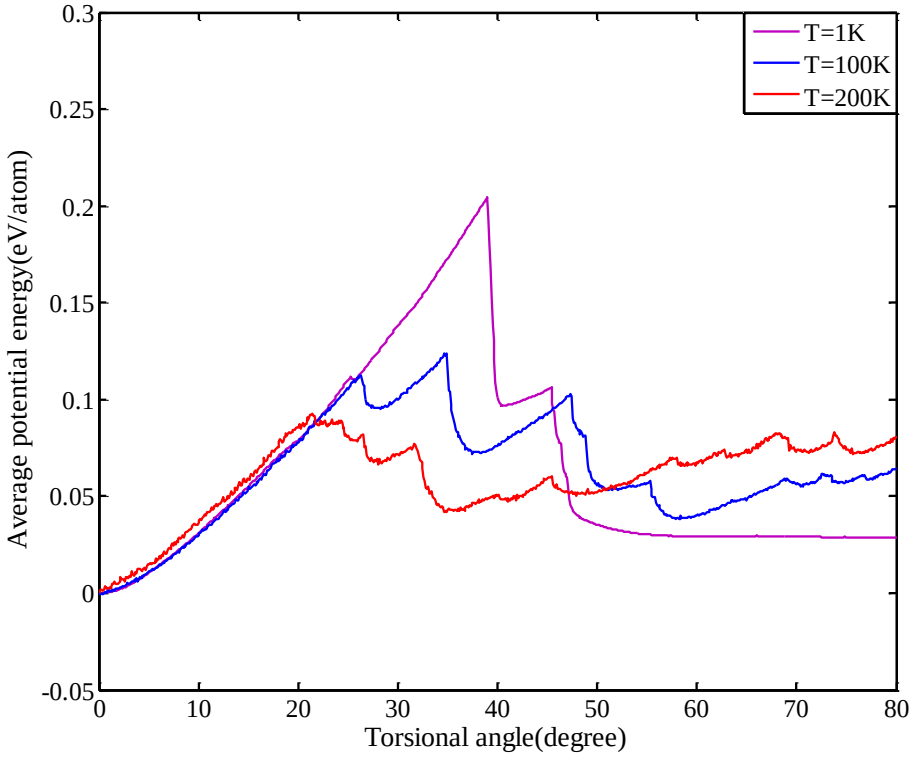

Fig. 10. The relationship between torsional angle and average potential energy at different simulation temperatures.

3.4. Loading rate

In order to obtain further insights into the torsional properties of BN nanocones, the loading rate in MD simulation should be taken into consideration. Thus, expect the loading rate with 0.01degree/ps in previous simulations, another two loading rates with 0.005degree/ps and 0.02degree/ps were carried out in the simulations to investigate the influences of loading rate on torsional properties of BN nanocones. For simplification and without loss generality, the models in simulations are chosen as 30Å cone hight and 120 °disclination angle. The average torque and potential energy for different loading rates are shown in Figs. 11 and 12, respectively. It is noted that, for three kinds of loading rates, the tendency of the curves for the relationships between torsional angle and average torque and potential energy are similar. The main influence of

loading rate on the torsional properties of BN nanocones is the failure torsion angles. It can be seen that the failure torsion angle decreases with the increasing loading rate. This inidcates that the higher the loading rate is, the earlier fracture of the nanocone occurs. This observation is in good agreement with previous studies for the nanostructures [28]. The reason is mainly due to the high stress concentration under the high loading rate condition. However, it must be pointed out that the maximum failure torque and average potential energy are almost the same when the loading rate changes. Thus, it can be concluded that the torsional properties of BN nanocones are loading rate dependent. Nevertheless, it is feasible that the loading ratio 0.01 degree/ps in the previous simulations is chosen for the consideration of simplification.

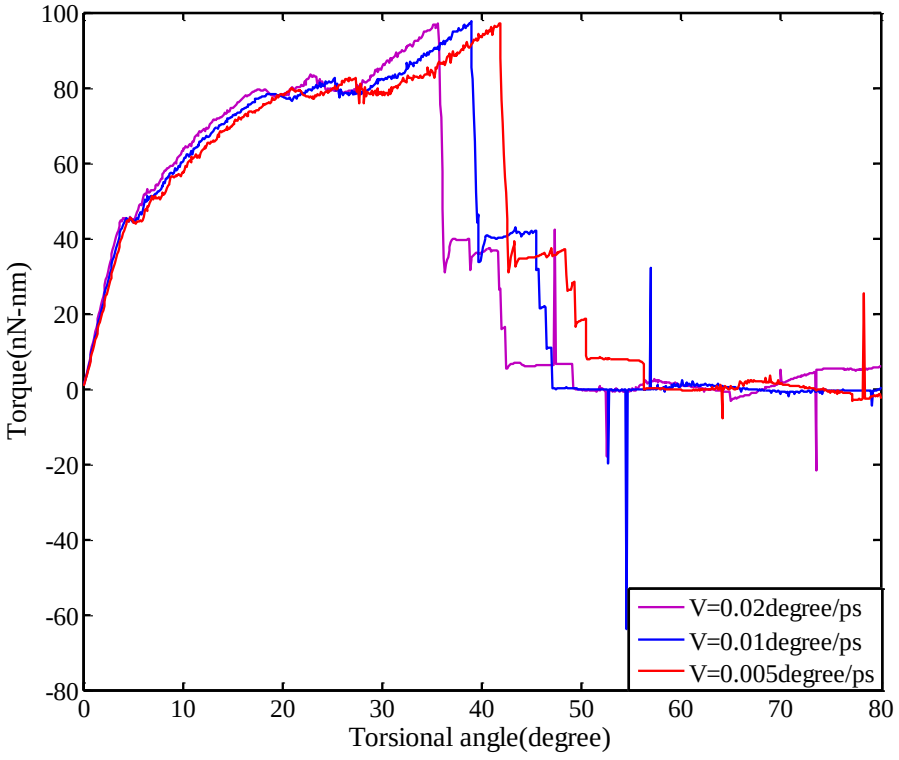

Fig. 11. The relationship between torsional angle and torque at different loading rates.

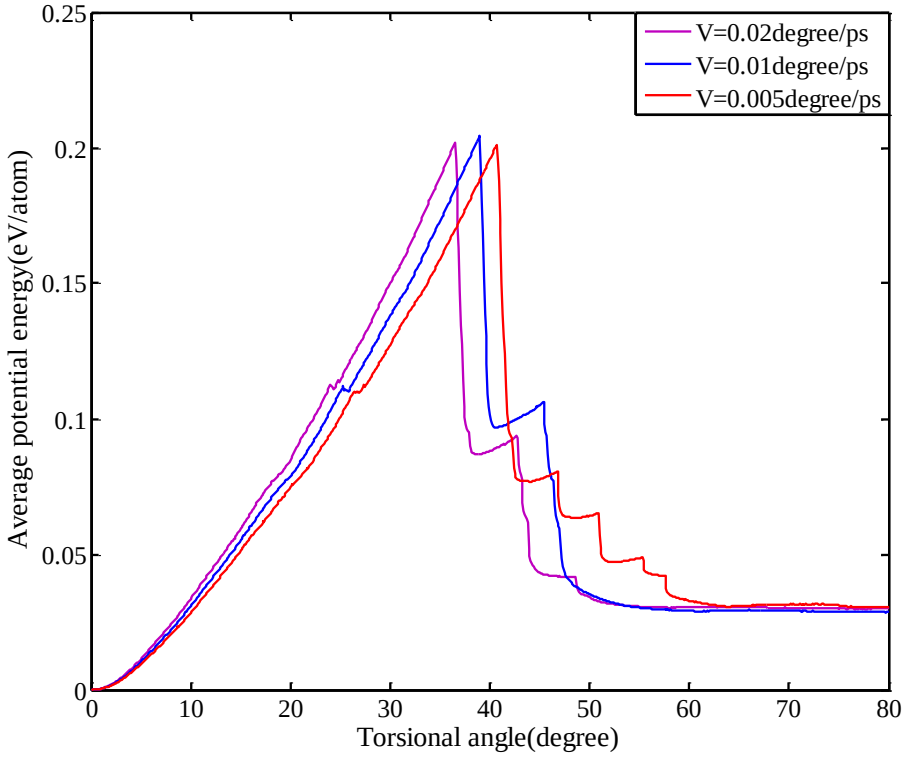

Fig. 12. The relationship between torsional angle and average potential energy at different loading rates.

4. Conclusions

The twist process of BN nanocones has been tracked by MD simulations, which was used to investigate the torsional response on single-walled BN nanocones. When the BN nanocone is twisted, it will lose its cone geometry and buckle into a twisted screw shape, torque and average potential energy increase with the torsion angle increasing until torsion angle reaches to the failure point and then decrease quickly. The torque and average potential energy decrease with the increasing cone height and disclination angle, and the failure torsion angle increases with the increasing cone height and disclination angle. In addition, torsional behavior of BN nanocones at different simulation temperatures also has been investigated. With the temperature increasing, the

influence of thermal fluctuation becomes serious, and the structure of nanocones changes more quickly due to the frequent break and rearrangement of atomic bonds, also the toque and average potential energy of nanocones decrease as the simulation temperature increases. Meanwhile, through simulations of different loading rates it can be found that the loading rate also affects torsional property in some degree. These obtained results of torsional behavior for different cone heights, disclination angles, simulation temperatures and loading rates can provide the advanced knowledge of BN nanocones for their potential applications.

Acknowledgements

This research was supported by National Natural Science Foundation of China (Nos. 51175372, 51405333), Reserved Academic Program of Peiyang Scholar, and Program for New Century Excellent Talents in University (No. NCET -11-0374).

References

[1] M. L. Liao, “Buckling behaviors of open-tip carbon nanocones at elevated temperatures,” Applied Physics A, 117(3), 1109-1118(2014).

[2] A. K. Geim, K. S. Novoselov, “The rise of grapheme,” Nature Material, 6(3), 183-191(2007).

[3]A. Gali, “Ab initio study of nitrogen and born substitution impurities in single-wall SiC nanotubes,” Physical Review B, 73(24), 5415-5424(2006).

[4] C. Wang, Y. Zhang, Y. Xiang, “Recent studies on bucking of carbon nanotubes,” Applied Mechanics Reviews, 63(3), 0804-0822(2010).

[5] J. Feliciano, C. Tang, Y. Y. Zhang, et al, “Aspect ratio dependent bucking mode transition in single-walled carbon nanotubes under compression,” Journal of Applied Physics, 109(8), 4323-4328(2011).

[6] A. Krishnan, E. Dujardin, M. Treacy, et al, “Graphitic cones and the nucleation of curved carbon surfaces,” Nature, 388(6641), 451-454(1997).

[7] T. H. Chang, Y. Zhu, “A microelectromechanical system for thermomechanical testing of nanostructures,” Applied Physics Letters, 103(26), 31141-31145(2013).

[8] C. Q. Qu, L. Qiao, “First-principles density-functional calculations on the field emission properties of BN nanocones,” Solid State Communications, 146(9-10), 399-402(2008).

[9] L. Bourgeois, Y. Bando, W.Q. Han, et al, “Structure of boron nitride nanoscale cones: Ordered stacking of 240 degrees and 300 degrees disclinations,” Physics Review B, 61(11), 7686-7691(2000).

[10]M. Terauchi, M. Tanaka, K. Suzuki, et al, “Production of zigzag-type BN nanotubes and BN cones by thermal annealing,” Chemical Physics Letters, 324(5-6), 359-364(2000).

[11] C. Y. Zhi, Y. Bando, C. C. Tang, et al, “Large-scale fabrication of boron nitride nanohorn,” Applied Physics Letters, 87(6), 063107(2005).

[12] G. C. Loh, S. Nigam, G. Mallick, et al, “Carbon-Doped Boron Nitride Nanomesh: Stability and Electronic Properties of Adsorbed Hydrogen and Oxygen,” Journal of Physical Chemistry C, 118(41), 23888-23896(2014).

[13] Z. Xu, D. Golberg, Y. Bando, “Electrical field-assisted thermal decomposition of boron nitride nanotubes,” Chemical Physics Letters, 480(1-3), 110-112(2009).

[14] M. Mirzaei, M. Yousefi, M. Meskinfam, “Chemical shielding properties for BN, BP, A l N, and A l P nanocones: DFT studies,” Superlattices and Microstructures, 51(6), 809-813(2012).

[15] L. Boldrin, F. Scarpa, R. Chowdhury, et al, “Effective mechanical properties of hexagonal boron nitride nanosheets,” Nanotechnology, 22(50), (2011).

[16] S. Azevedo, M. S. C. Mazzoni, R. W. Nunes, et al, “Stability of antiphase line defects in nanometer-sized boron nitride cones,” Physics Review B, 70(20), 205412 (2004).

[17] C. Zhi, Y. Bando, C. Tang, et al, “Electronic structure of boron nitride cone-shaped nanostructures,” Physics Review B, 72(24), 245419 (2005).

[18] C. Y. Zhi, N. Hanagata, Y. Bando, et al, “Dispersible Shortened Boron Nitride Nanotubes with Improved Molecule-Loading Capacity,” Chemistry-an Asian Journal, 6(9), 2530-2535(2011).

[19] L. Bourgeois, Y. Bando, W. Q. Han, et al, “Structure of boron nitride nanoscale cones: Ordered stacking of 240° and 300° disclinations,” Physics Review B, 61(11), 7686-7691(2000).

[20] D. Pedreira, S. Azevedo, M. Machado, “Electronic properties of boron nitride nanocones under the influence of parallel and perpendicular external electric fields,” Physics Review B, 78(8), 085427 (2008).

[21] M. Machado, I. A. Larkin, P. Piquini, “Electronic and structural properties of two mirrored boron-nitride nanocones with 240 degrees disclination,” Brazilian journal of physics, 39(1A), 239-241(2009).

[22] M. Machado, P. Piquini, R. Mota, “Charge distributions in BN nanocones: electric field and tip termination effects,” Chemical Physics Letters, 392(4-6), 428-432(2004).

[23] W.H. Moon, H.J. Hwang, “Molecular-dynamics simulation of structure and thermal behavior of boron nitride nanotubes,” Nanotechnology, 15(5), 431-434(2004).

[24] A. Mudi, C. Chakravarty, “Effect of Berendsen thermostat on the dynamical properties of water,” Molecular Physics, (102)7, 681-685(2004).

[25] M. L. Liao, Y. C. Wang, S. P. Ju, et al, “Deformation behaviors of an armchair born nitride nanotubes under tensile strains,” Journal of Applied Physics, 110(5), 054310-054316(2011).

[26] M. M. S Fakhrabadi, N. Khani, R. Omidvar, et al, “Investigation of elastic and buckling properties of carbon nanocones using molecular mechanics approach,” Computational Materials Science, 61, 248-256(2012).

[27] Y. Y. Zhang, C. M. Wang, Y. Xiang, “A molecular dynamics investigation of the torsional responses of defective single-walled carbon nanotubes,” Carbon, 48(14), 4100-4108(2010).

[28] A. R. Khoei, E. Ban, P. Banihashemi, “Effects of temperature and torsion speed on torsional properties of single-walled carbon nanotubes,” Materials Science and Engineering C , 31(2), 452-457(2011).